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(71) Applicant *(for all designated States except US)*: CONDUCTUS, INC. [US/US]; 969 Maude Avenue, Sunnyvale, CA 94086 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : NEWMAN, Nathan [US/US]; 8149 Cabrillo Highway, Montara, CA 94037 (US). CHAR, Kookrin [KR/US]; 704 Chimalus Drive, Palo Alto, CA 94306 (US).

(74) Agent: JACOBS, Marvin, E.; 2151 Alessandro Drive, Suite 215, Ventura, CA 93001 (US).

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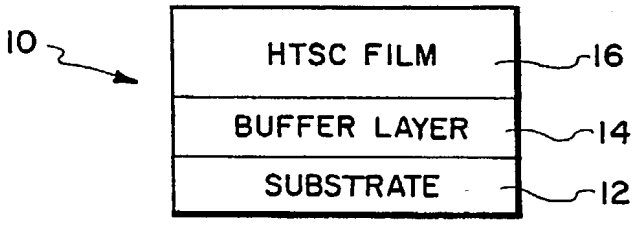

(57) Abstract

High temperature superconducting layered structures for use in microwave applications are fabricated by depositing a thin film of epitaxial buffer (14) such as strontium titanate or calcium titanate by a deposition process such as laser ablation on a low loss sapphire substrate (12) followed by depositing an in-situ grown film of high temperature superconductor (16) such as $Y_1Ba_2Cu_3O_7$ on the buffer layer. The YBCO film has low surface resistance and a narrow transition temperature.

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DESCRIPTION

HIGH TEMPERATURE SUPERCONDUCTING FILMS ON ALUMINUM OXIDE SUBSTRATES

Cross Reference To Related Applications

This application is a continuation-in-part of Serial Number 494,730 filed March 16, 1990, Serial Number 495,568 filed March 16, 1990 and Serial Number 565,691 filed August 13, 1990.

Technical Field

This invention relates to high critical temperature superconducting (HTSC) films and, more particularly, this invention relates to the preparation of HTSC films on sapphire (aluminum oxide) substrates by the use of stable, epitaxial buffer layers.

Background of the Invention

The recent discovery of high critical temperature superconducting materials has created interest in the use of these materials in microwave devices. The HTSC metal cuprate materials cannot readily be produced in bulk with geometries and properties suitable for microwave devices. Presently, devices based on the HTSC materials are fabricated by formation of thin films on substrates by techniques similar to those used to fabricate semiconductor devices. To be useful in a microwave device the HTSC film must be grown on a substrate having low dielectric losses at high frequencies.

Silicon, a readily used substrate for semiconductor devices, cannot be used with the HTSC cuprate materials since at the temperature prevalent during deposition the cuprate reactants readily react with silicon. Sapphire (Al_2O_3) would appear to be an excellent substrate since it has a very low dielectric loss and is a strong, low cost, highly crystalline material available commercially in large sizes. Sapphire would be a good substrate for bolometer (infrared detector) applications since thin films of sapphire have low heat capacity. Epitaxial films of a HTSC

material such as $YBa_2Cu_3O_7$ can be grown on sapphire substrates. However, the optimum window of substrate temperatures during film deposition is relatively narrow [4]. At high temperatures above about 700 K, the $YBa_2Cu_3O_7$ thin film reacts with the sapphire, especially the Ba atoms. At low temperature, below about 650 K, it is very difficult to produce thin $YBa_2Cu_3O_7$ films having good epitaxy.

There are other substrate materials that provide epitaxial growth of thin HTSC films with high superconducting transition temperatures and low rf surface resistance, such as strontium titanate ($SrTiO_3$), calcium titanate ($CaTiO_3$), lanthanum aluminate ($LaAlO_3$), magnesium oxide (MgO) and yttria stabilized zirconia (YSZ). However, thick substrates of some of these materials, e.g. strontium or calcium titanate, exhibit too high an rf loss or do not have high enough strength to act as a substrate for large area microwave devices. Some of these materials are only available in small sizes and/or at very high cost.

However, thin epitaxial films of these materials exhibit a low dielectric loss and would be useful as a buffer layer between the HTSC film and the sapphire substrate if they provided an epitaxial surface for the HTSC film and were stable and non-reactive with the HTSC film and the substrate.

List of References

1. Multilayer $YBa_2Cu_3O_x$ - $SrTiO_3$ - $YBa_2Cu_3O_x$ Films For Insulating Crossovers, Kingston et al., Applied Physics Letters, January 8, 1990.

2. $YBa_2Cu_3O_7$ Films Grown on Epitaxial MgO Buffer Layers on Sapphire, Talvacchio et al., Proceedings M^{2}S-HTSC, Stanford, July 1989, Physica.

3. The Sputter Deposition and Characterization of Epitaxial Magnesium Oxide Thin Films and Their Use as a Sapphire/ YBCO Buffer Layer, Morris et al., Proc. M.A.S. Vol 169, 1990.

4. Properties of Epitaxial $YBa_2Cu_3O_7$ Thin Films on Al_2O_3 {1012}, Char et al., Appl. Phys. Lett. 56(8) 19 Feb 1990, p.785-787.

Statement of the Prior Art

Kingston et al. [1] disclose the use of $SrTiO_3$ as an insulating layer between two $YB_2Cu_3O_x$ films, one of which was deposited on an MgO substrate. MgO is not the best substrate for microwave applications due to its high dielectric loss. MgO does not provide a fully compatible lattice match with HTSC films such as $YBa_2Cu_3O_7$ and polished MgO surfaces degrade in air with humidity. Talvacchio et al. [2] grew $YBa_2Cu_3O_7$ films on epitaxial MgO buffer layers on sapphire. This layered structure failed as a microwave device since the MgO was excessively moisture sensitive. The HTSC film did not have sufficient orientation and there were too many random grains. Morris et al. [3] formed an MgO buffer layer by sputter deposition at 5.5 to 7 Pa (about 40-50 m Torr) a fairly low pressure. The resulting YBCO film grown on the epitaxial MgO has high normal state resistance and a broad superconducting transition.

Statement of the Invention

The invention provides a HTSC buffer layered structure on sapphire that is stable and suitable for microwave environments or for use in the fabrication of bolometers. The layered structure with a thin $SrTiO_3$ or $CaTiO_3$ buffer layer has a sharp transition and good thermal response, making it suitable for bolometer applications. The HTSC film can be grown over a wide temperature range without the HTSC reacting with the sapphire substrate or the buffer reacting with the substrate or the HTSC film. The layered structures of the invention provides the highest microwave performance of any sapphire supported HTSC film reported to date. Others have reported surface resistance measuring on a par with copper. The layered sapphire supported HTSC structure of the invention exhibits rf surface resistance 2 to 3 times better than copper at 10 GHz and 77 K and much better than copper at lower temperatures. The YBCO films grown on the buffer layer exhibit low normal state resist-

ance and a narrow superconducting transition.

The buffer layer in the HTSC structure of the invention is grown in a high pressure process such as laser ablation, sputtering or metallo-organic compound vapor deposition (MOCVD). Talvacchio et al. [2] used electron beam deposition of the MgO film. Electron beam epitaxial deposition is conducted at relatively high vacuum, about 10^{-5} Torr. The low partial pressure of oxygen is believed to result in an oxygen deficient buffer layer film. These films are chemically active and react with water which degrades the quality of the overlying HTSC film. The buffer layer in the process of the invention is deposited at higher pressure which results in inert buffer layers with good epitaxial qualities. The $SrTiO_3$ and $CaTiO_3$ buffer layers are excellent intermediate substrates for forming high performance, stable HTSC films.

These and many other objects and attendant advantages of the invention will become apparent as the invention becomes better understood by reference to the following and detailed descriptions when considered in conjunction with the accompanying drawings.

Brief Description of the Drawings

Figure 1 is a schematic drawing of a layered HTSC-Buffer-Sapphire structure produced according to the process of this invention;

Figure 2 is a series of curves showing Surface Resistance, R_s of epitaxial $YBa_2Cu_3O_7$ films as a function of temperature at 10 GHz;

Figure 3 is a series of plots of Surface Resistance, R_s vs. frequency with Cu data at 77 K and Nb data at 7.7 K;

Figure 4(a) is a c-axis scan of the $YBa_2Cu_3O_7$ film;

Figure 4(b) is a ϕ-axis scan of the [103] peak of the $YBa_2Cu_3O_7$ film;

Figure 5(a) is the mutual inductance response of the $YBa_2Cu_3O_7$ film at 1 mA;

Figure 5(b) is the mutual inductance response of the

$YBa_2Cu_3O_7$ film at 100 mA; and

Figure 6 is a graph of surface resistivity, R_s versus temperature.

Detailed Description of the Invention

Referring now to Figure 1, the layered structure 10 is composed of a sapphire base or substrate 12, a thin buffer layer 14 and a HTSC layer 16. The buffer layer 14 and the HTSC layer 16 may be laid down in a pattern to form a device by use of a mask formed by conventional lithographic techniques or by use of shutters or shields.

Sapphire substrates are commercially available in high purity and in a variety of thicknesses and shapes. The support need only have sufficient thickness such as 0.1 millimeters to provide a mechanically strong substrate. Substrates having thicknesses above 1.0 millimeters would usually not be utilized since they add cost and weight to the device without providing any other benefit.

The buffer layer is an epitaxial layer having sufficient thickness such that the growth of HTSC film is influenced solely by the buffer layer and not by the sapphire substrate. The buffer layer can have a minimum thickness of a monolayer or less. However, it is preferred that the buffer layer cover the sapphire surface and any anomalies on the surface and suitably has a thickness of at least 50 Angstroms. Thicknesses above about 3000 Angstroms are unnecessary and may interfere with the microwave device. The buffer can be formed from crystalline materials having a close epitaxial match to the HTSC material such as strontium titanate, calcium titanate, lanthanum aluminate, magnesium oxide or yttrium stabilized zirconia (YSZ). Strontium titanate and calcium titanate are preferred since it appears that they form the best HTSC films.

In the process of the invention, the thin layer of buffer is formed by deposition in a chamber having a high percentage, usually from 10 to 100% of oxygen. The pressure in the chamber is higher than practiced in the elec-

tron beam deposition process and in other deposition processes. The pressure in the chamber is at least 40 m Torr and can be as high as 10 Torr, usually about 100 to 500 m Torr. The buffer layer may be formed by a variety of vapor deposition techniques such as on- or off-axis sputtering, metallo-organic vapor deposition (MOCVD) or laser ablation.

Laser ablation is preferred since it appears to provide a buffer layer that provides the highest quality HTSC films. This may be due to several factors. Laser ablation is conducted at a fairly high pressure. The deposition chamber contains from 20 to 100% oxygen at a pressure typically from 100 m Torr up to several Torr. The higher oxygen pressure could provide a more stable, more perfect crystalline epitaxial layer. Laser ablation generates its own plasma. The charged ionic species may assemble into a more ordered crystal form. The laser is pulsed during laser ablation. During the non-pulsed period the growing crystal can relax to allow the metal and oxygen atoms to assume their positions in the crystal lattice of strontium titanate or calcium titanate.

The HTSC film is preferably grown by off-axis sputtering, laser ablation or MOCVD. Any of these procedures can be used to form the buffer layer. A common chamber can be used to form the buffer layer and HTSC film by two consecutive laser-ablation depositions or two consecutive off-axis sputtering depositions.

In off-axis sputtering the sapphire substrate or the buffer layer coated sapphire substrate is placed on a heated substrate holder in a sputtering chamber at an angle of at least 40°, usually 90°, from the sputtering source. The substrate is heated to a temperature of from about 650 K to 800 K. The chamber contains from 10-50% of an oxidizing gas such as oxygen or nitrous oxide. The vapor source is a composite ceramic in the correct stoichiometric ratio for the film such as a $Y_1Ba_2Cu_3$ alloy or a $SrTiO_3$ crystal or pressed powder source. Deposition is usually conducted over several hours at a high pressure between 100 and 500

Torr. A post deposition treatment in oxygen at a temperature from 400 K to 600 K can be conducted in case of the HTSC film.

The films of high critical temperature (T_c) superconducting materials (HTSC) prepared in the present invention are mixed metal cuprates or mixed metal bismuthates having a T_c above about 30 K, usually above 70 K which belong to four families: the rare earth cuprates, the thallium-based cuprates, the bismuth-based cuprates and the alkaline earth bismuthates. The HTSC materials have an ordered lattice and are usually crystalline ceramics of the general formula

$$M_x^1 M_y^2 Cu_z O_n$$

where M^1 is a Group IIIA metal, Group IIIB metal, Group VB or a rare earth metal, M^2 is a Group IIA metal and x, y, z and n are integers. Usually the ratio of y:x is about 2:1 and the ratio of z:x is at least 3 usually from 3:1 to 6:1. The oxygen is present in an amount to satisfy valency of the metals and n is usually no more than 20, typically about 5-15.

M_1 can be a Group IIIA metal such as Yttrium (Y) or lanthanum (La), a Group IIIB metal such as Thallium (Tl), or Group VB metal such as Bismuth (Bi) or a rare earth metal such as Erbium (Er), Cerium (Ce), Praseodymium (Pr), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Ytterbium(Yb), Lutetium (Lu) or combinations of these metals. M^2 is a Group IIA metal such as strontium, barium, calcium or mixtures thereof.

The examples of practice of the invention will be directed to the YBaCuO materials of the general formula $Y_1Ba_2Cu_3O_7$, but the invention is equally applicable to other HTSC materials of the cuprate family or bismuthate family such as the bismuth cuprate of the general formula BiSrCaCuO or the thallium cuprate of the general formula TlBaCaCuO.

The invention will now be illustrated by specific examples. 500 Angstrom thick films of $YBa_2Cu_3O_7$ (123) were grown on 500 Angstrom thick buffer layers of $SrTiO_3$ or

$CaTiO_3$. The structural and electrical properties are characterized by x-ray diffraction data, SEM images and AC mutual inductance responses.

Both laser ablation and off-axis sputtering techniques were utilized in growing low surface resistance "123" films on Al_2O_3 with $SrTiO_3$ buffer layers. In the case of laser ablation about 1.8 Joule/cm^2 energy density of 248 nm wavelength pulsed excimer laser beam was focused on a $SrTiO_3$ or an "123" pellet. Other deposition parameters were 200 m Torr of oxygen pressure and 750 C substrate temperature. In the case of off-axis sputtering two sputtering guns were mounted face to face and the substrates were glued on a heater that faces perpendicular to the both $SrTiO_3$ and "123" targets. Oxygen pressure of 40 m Torr and Argon pressure of 160 m Torr were used at the substrate temperature of 740 C.

In order to measure surface resistance at microwave frequency a parallel plate resonator was formed by sandwiching two 1 cm by 1 cm "123" thin films face to face with a 12.5 μm thick Teflon dielectric in between. This resonator generates a series of transverse electromagnetic modes. The advantage of this method is that the current and field distribution can be calculated and the relation between the measured Q factor and the surface resistance R_s can be deduced in a straightforward fashion. This method has been successfully used to measure 20$\mu\Omega$ for Nb films at 4.2 K at 10 GHz. The resolution of this method is about 5 $\mu\Omega$at 10 GHz.

Figure 2 shows the temperature dependence of surface resistance R_s of the "123" films grown on $SrTiO_3$ buffer layers on Al_2O_3(1102) substrates. The circles denote the data on a pair of films made by laser ablation and the crosses represent the data on films grown by the off-axis sputtering technique. They have a residual resistance of about 65 $\mu\Omega$ at low temperature and about 800 $\mu\Omega$ at 77 K at 10 GHz. The actual resonance frequency (w) was about 11 GHz and the usual $R_s(w) \infty w^2$ relation was used to scale back to 10 GHz.

These surface resistance values are compared to those of Cu at 77 K and Nb at 7.7 K in Figure 3. The resistance range 65 to 200 $\mu\Omega$ between 10 K and 50 K is lower than the Nb 7.7 K value at 10 GHz. The 800 $\mu\Omega$ at 77 K is also at least a factor 10 better than that of Cu at 77 K.

For structural information x-ray diffraction data of a c-axis scan and a ϕ scan of the (103) peak are shown in Figures. 4a and 4b. The c-axis scan shows that the samples are well aligned in the c-axis direction. The existence of (200) peaks means that there are some a-axis oriented grains in the sample. A SEM (Scanning Electron Microscope) image reveals that these a-axis oriented grains reside on the surface mostly as isolated grains. The rocking curve of the (005) peak is about 2.4 degree wide, which is not much different from the epitaxial "123" films on bare sapphire.

The big difference in microstructure between epitaxial "123" thin films with $SrTiO_3$ buffer layer and films without $SrTiO_3$ buffer layer can be found in the ϕ-scan of (103) peak in Figure 4b. The sharp peaks every 90 degree means that the a-axis and b-axis are also aligned in the sapphire plane (1102). The full width at half maximum, $\hat{}\ \phi$, of the peaks in the ϕ-scan is about 3.8 degree. In comparison, $\hat{}\ \phi$ of good epitaxial films on MgO, $SrTiO_3$ is about 1.5 degree. However, unlike the data of the "123" thin films on bare sapphire [4], these peaks do not have the shoulders. In other words, the "123" films with a $SrTiO_3$ buffer layer have better in-plane epitaxy than those without a $SrTiO_3$ buffer layer.

It is known that the I-V characteristics of the grain boundary of two misaligned grains have Josephson junction behavior. It was further found by a weakly coupled grain model that these grain boundaries lead to higher surface resistance as well as longer penetration depth. Improved in-plane epitaxy can be interpreted as reduction of grain boundaries, which results in lower surface resistance.

The mutual inductance response of a film as a function

of temperature is shown in Figures 5a and 5b. It was measured at 1 kHz with a maximum magnetic field of 0.6 Gauss on the film surface. The 86.5 K, where the mutual inductance transition starts, is in good agreement with the temperature where the dc resistivity goes to zero.

Low surface resistance 65 $\mu\Omega$ at 4.2 K and 800 $\mu\Omega$ at 77 K at 10 GHz were exhibited by the epitaxial $YBa_2Cu_3O_7$ films on 500 Å thick buffer layers of $SrTiO_3$ on Al_2O_3 {1102} substrates. Improved microwave surface resistance data are believed to be the results of better in-plane epitaxy due to the presence of the $SrTiO_3$ buffer layer.

Strontium titanate has some reactivity with the components of the growing HTSC film limiting the temperature that can be used during growth of the HTSC film to about 760°C. High quality HTSC film can be grown at higher temperature.

Though strontium titanate has a lattice spacing of about 3.92 Angstroms which is close to the approximate 3.9 Angstroms lattice spacing of $YBa_2Cu_3O_{7-x}$, it is far from the lattice spacing of sapphire (about 3.5 Angstroms). This lattice mismatch can cause some grains to grow in undesired directions.

Strontium titanate buffers are usually deposited in a thickness of at least 100 Angstroms which increases microwave losses and is not conducive to the formation of the smoothest HTSC films.

Higher quality HTSC thin films are produced in accordance with the invention on calcium titanate substrates. The calcium titanate can be a bulk substrate or a thin buffer film or a substrate of different composition such as silicon or sapphire.

Calcium titanate has a lattice spacing of about 3.82 Angstroms which is intermediate to the lattice spacing of $YBa_2Cu_3O_{7-x}$ (~ 3.9 Angstroms) and sapphire (~ 3.5 Angstroms). Calcium titanate films can be grown with less strain. Thinner films have less dislocations and crystal defects. Epitaxial films of calcium titanate which are 100 Angstroms

in thickness or less provide excellent substrates for growing thin HTSC films. Thinner buffer films provide lower microwave losses.

Furthermore, since calcium titanate is less reactive with the ions forming the HTSC film, the deposition temperature can be substantially higher, e.g. about 800°C which contributes to the quality and performance of the HTSC film. Preliminary measurements indicate that the critical current density of the HTSC film are about 2 times better than comparable films grown on strontium titanate buffer films on sapphire.

Figure 6 illustrates the data from 3 different measurements of the surface resistance of 500 Angstrom thick 123 YBCO films grown on 100 Angstrom thick $CaTiO_3$ buffer layers. The surface resistivity was scaled to 10 GHz.

In a measurement of x-ray scattering, it was found that the full width at half maximum, ϕ, of the peaks in the ϕ-scan is about 3.8 degree. In comparison, ϕ of good epitaxial films on MgO or $SrTiO_3$ is about 1.5 degree. However, unlike the data of the "123" thin films on bar sapphire [4], these peaks do not have the shoulders. In other words, the "123" films with a $CaTiO_3$ or $SrTiO_3$ buffer layer have better in-plane epitaxy than those without a $CaTiO_3$ or $SrTiO_3$ buffer layer.

It is known that the I-V characteristics of the grain boundary of two misaligned grains have Josephson junction behavior. It was further found by a weakly coupled grain model that these grain boundaries lead to higher surface resistance as well as longer penetration depth. Improved in-plane epitaxy can be interpreted as reduction of grain boundaries, which results in lower surface resistance.

The mutual inductance response of a film as a function of temperature was measured at 1 kHz with a maximum magnetic field of 0.6 Gauss on the film surface. At 86.5 K, the temperature where the mutual inductance transition starts, is in good agreement with the temperature where the dc resistivity goes to zero.

Improved microwave surface resistance data and critical current density are believed to be the results of better in-plane epitaxy due to the use of the $CaTiO_3$ buffer layer.

It is to be realized that only preferred embodiments of the invention have been described and that numerous substitutions, modifications and alterations are permissible without departing from the spirit and scope of the invention as defined in the following claims.

WHAT IS CLAIMED IS:

1. A superconducting structure comprising:

a sapphire substrate;

a thin buffer layer of strontium titanate or calcium titanate deposited on a surface of the substrate; and

a thin film of high temperature superconductor deposited on a surface of the buffer layer.

2. A structure according to claim 1 in which the film is in the form of a pattern.

3. A structure according to claim 2 in which the buffer layer has a thickness of at least 50 Angstroms.

4. A structure according to claim 3 in which the film has a thickness of at least 100 Angstroms.

5. A structure according to claim 4 in which the superconductor is a mixed metal cuprate or bismuthate.

6. A structure according to claim 5 in which the superconductor is $Y_1Ba_2Cu_3O_7$.

7. A superconducting structure comprising a thin film of high temperature superconductor deposited on the surface of calcium titanate.

8. A structure according to claim 7 in which the calcium titanate is a bulk substrate.

9. A structure according to claim 7 in which the calcium titanate is a thin buffer deposited on a substrate.

10. A structure according to claim 9 in which the substrate has low dielectric loss.

11. A structure according to claim 10 in which the substrate is sapphire.

12. A method of fabricating a high temperature superconducting device comprising the steps of:

depositing an epitaxial buffer layer of strontium titanate or calcium titanate on a sapphire substrate; and

growing a film of high temperature superconductor on the surface of the buffer layer.

13. A method according to claim 12 in which the deposition is effected by laser ablation or off-axis sputtering.

14. A method according to claim 12 in which the deposition is conducted in an oxidizing atmospher at a pressure of at least 40 m Torr.

15. A method according to claim 12 in which the superconductor is a mixed metal cuprate or bismuthate.

16. A method according to claim 15 in which the superconductor is $Y_1Ba_2Cu_3O_7$.

17. A device produced by the method of claim 12.

18. A device according to claim 17 in which the buffer is strontium titanate or calcium titanate, the substrate is sapphire and the film is $Y_1Ba_2Cu_3O_7$.

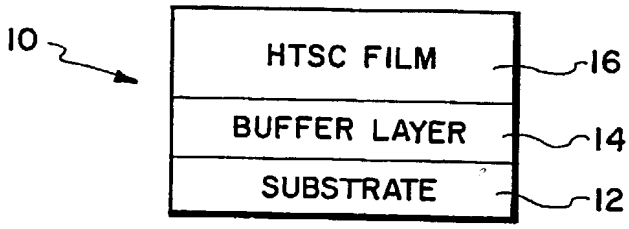


Fig. 1.

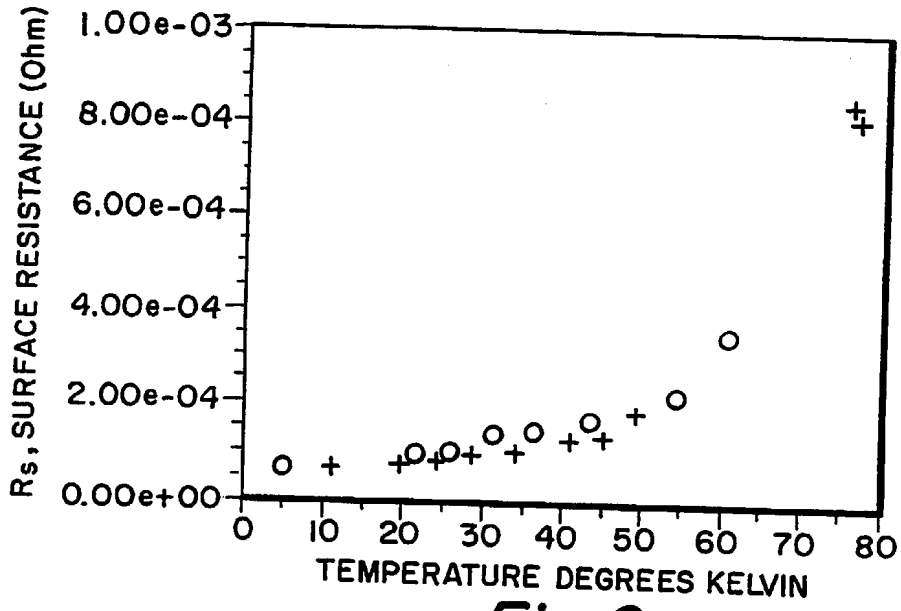


Fig. 2.

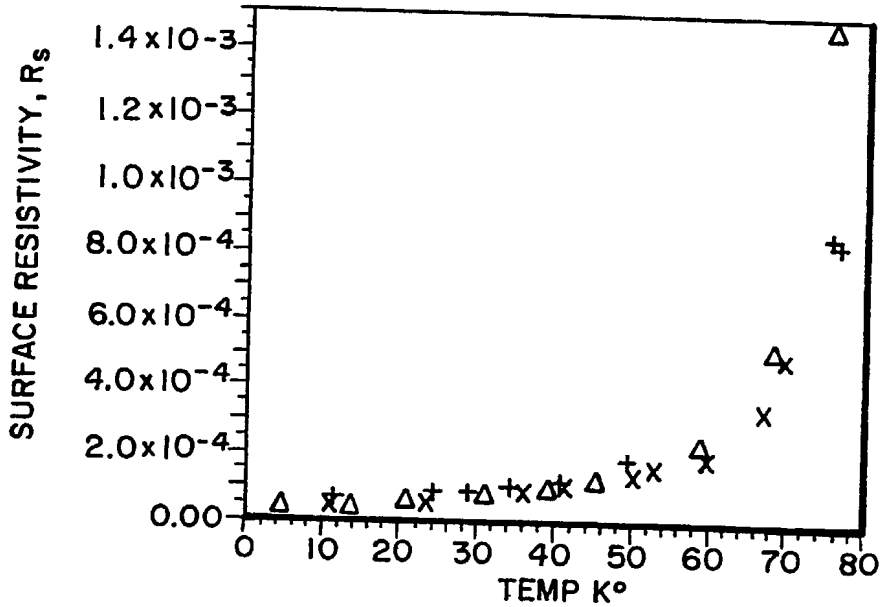


Fig. 6.

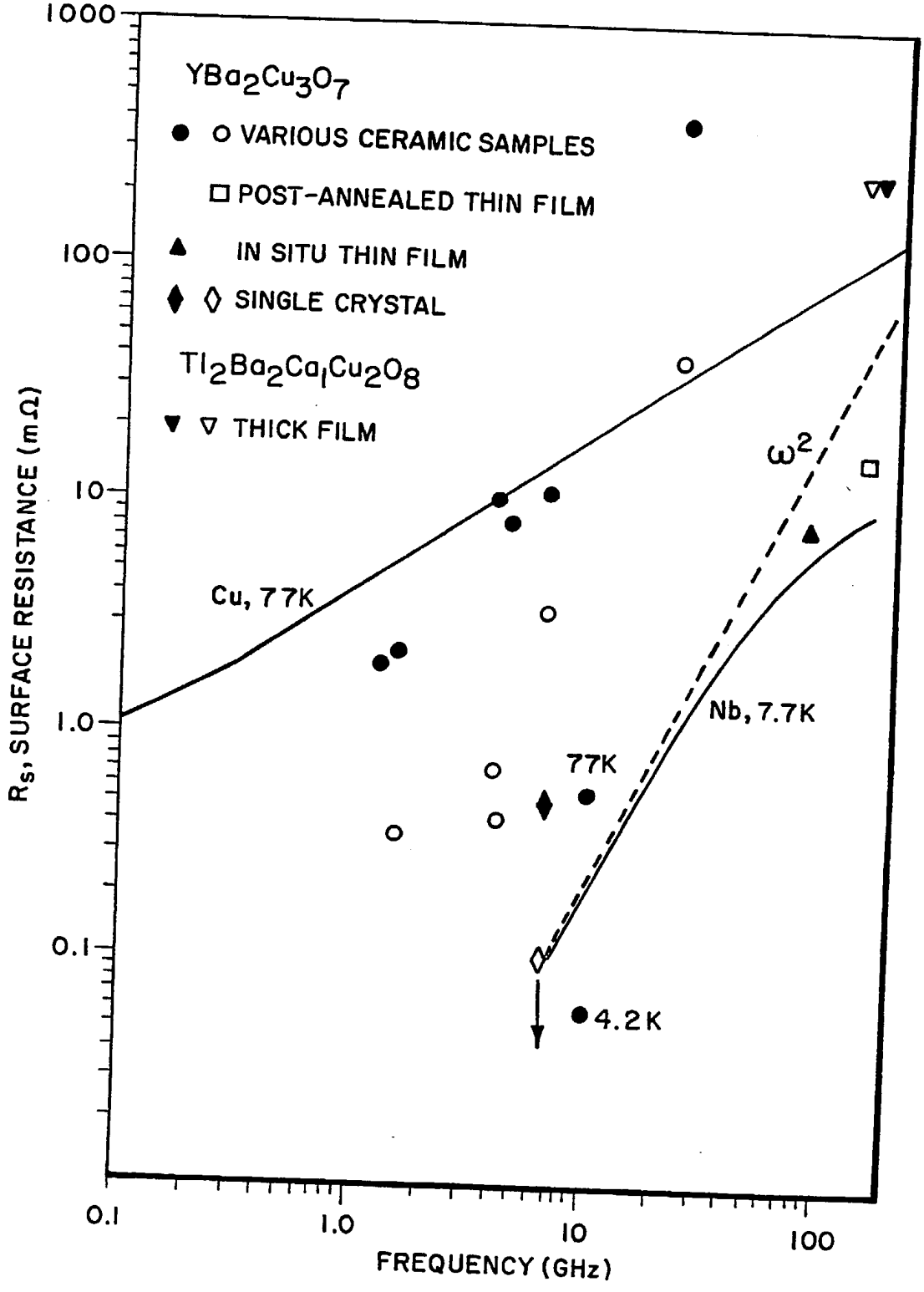
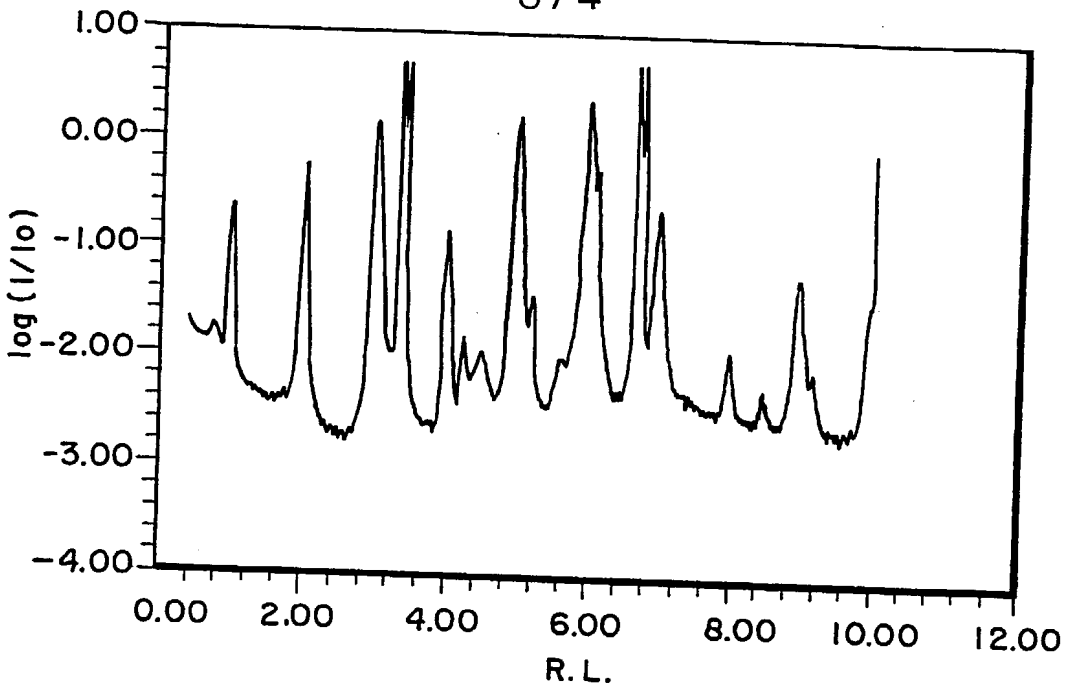

1000
100
10
1.0
0.1
R_s, SURFACE RESISTANCE (m Ω)
$YBa_2Cu_3O_7$
● ○ VARIOUS CERAMIC SAMPLES
□ POST-ANNEALED THIN FILM
▲ IN SITU THIN FILM
♦ ◇ SINGLE CRYSTAL
$Tl_2Ba_2Ca_1Cu_2O_8$
▼ ▽ THICK FILM
ω^2
Cu, 77K
Nb, 7.7K
77K
4.2K
0.1
1.0
10
100
FREQUENCY (GHz)

Fig. 3.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log (I/Io)
0.00
2.00
4.00
6.00
8.00
10.00
12.00
R. L.

Fig. 4a.

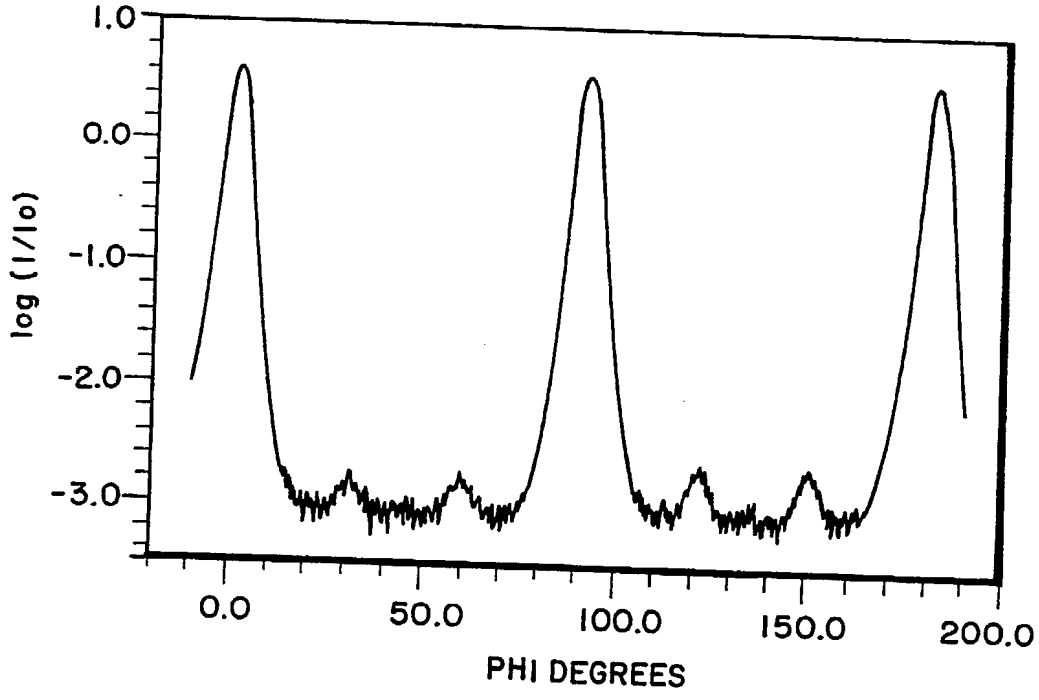
1.0
0.0
-1.0
-2.0
-3.0
log (I/Io)
0.0
50.0
100.0
150.0
200.0
PHI DEGREES

Fig. 4b.

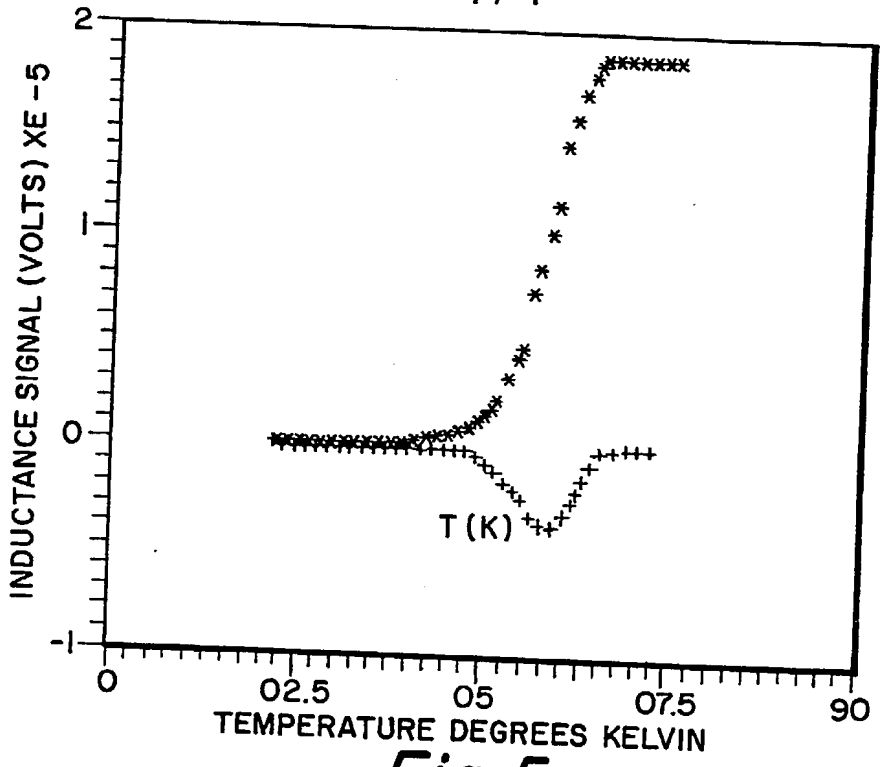
2
1
0
-1
INDUCTANCE SIGNAL (VOLTS) XE -5
T (K)
0
02.5
05
07.5
90
TEMPERATURE DEGREES KELVIN

Fig. 5a.

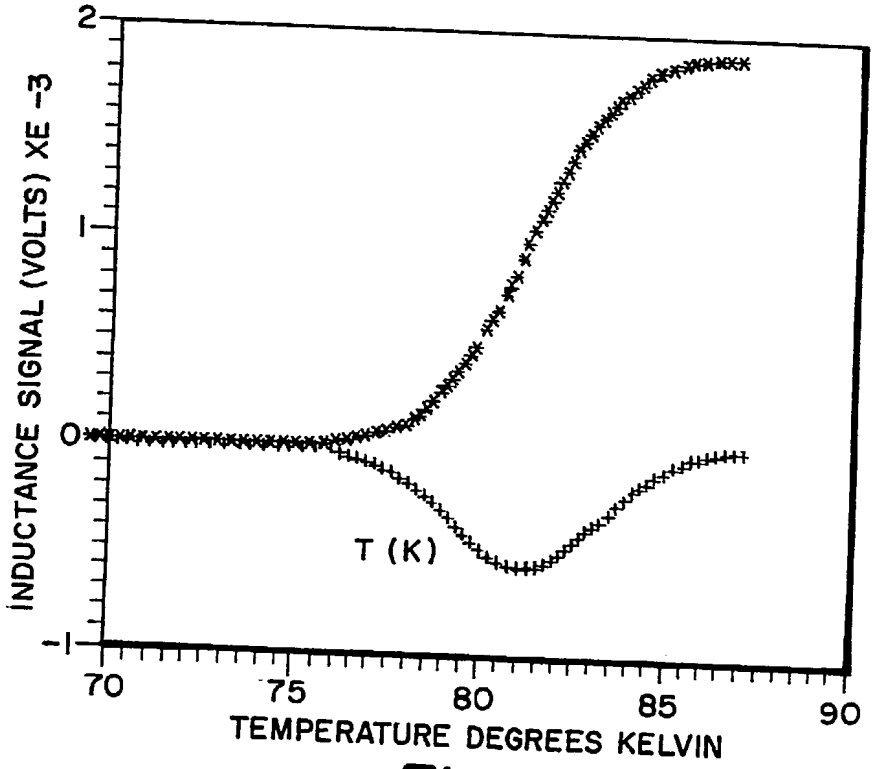
2
1
0
-1
INDUCTANCE SIGNAL (VOLTS) XE -3
T (K)
70
75
80
85
90
TEMPERATURE DEGREES KELVIN

Fig. 5b.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/01788

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): C30B 25/04
U.S. CL: 156/610

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S. CL.	156/610,611,613,614 565/1,729,730,731,732

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	US, A, 4,874,741 (SHAW ET AL) 17 October 1989.	
A,P	US, A, 4,920,094 (NOGAWA ET AL.) 24 April 1990.	
A,P	US, A, 4,943,558 (SULTIS ET AL) 24 July 1990	
A,P	US, A, 4,950,642 (OKAMOTO ET AL) 21 August 1990.	
Y	Applied Physics Letters, Vol. 52 (20) 16 May 1988, Stamper et al., "Sputter deposition of YBaCuOcn alumina and the influence of ZrO_2 buffer layers" pages 1746 to 1748, (Note pages 1746 and 1747).	1 to 18
Y	Applied Physics Letters, 08 January 1990, Kingston et al., "Multilayer YBa_2Cu_3Ox-Sr TiO_3-$YBa_2Cu_3O_x$ films for insulating Cross-overs", pages (1 to 9), (Note, pages 3 and 4).	1 to 18
A	EP, A, 0,322,619 (ASEA ET AL) 05 July 1989	

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
06 JUNE 1991	21 AUG 1991
International Searching Authority	**Signature of Authorized Officer**
ISA/US	ROBERT KINEMUND